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DEACTIVATION OF HF ($v = 1, 2$) BY FLUOROETHYLENES

S.J. Arnold

G. H. Kimbell

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DEACTIVATION OF HF (v=1,2) BY FLUOROETHYLENES.

by

10 S.J. Arnold G.H. Kimbell

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RESUME

La désactivation de HF(v=1,2) a été mesurée par la technique du tube d'écoulement à décharge. Les taux efficaces de désactivation vibrationnelle de HF(v=1,2) relaxé par C₂H₄, C₂H₃F, 1, 1C₂H₂F₂, cis 1, 2C₂H₂F₂, trans 1, 2C₂H₂F₂, C₂HF₃ et C₂F₄ ont été déterminés. Pour HF(v=1), le taux de relaxation va de 4.9x10⁴ s⁻¹ torr⁻¹ avec C₂H₄ à 3.5x10³ s⁻¹ torr⁻¹ avec C₂F₄; pour HF(v=2), il va de 1.3x10⁵ s⁻¹ torr⁻¹ à 8.8x10³ s⁻¹ torr⁻¹. La section efficace de collision pour la désactivation de HF(v=1) et HF(v=2) par C₂H₄ et les fluoroéthylènes varie linéairement avec le nombre d'atomes d'hydrogène. (NC)

ABSTRACT

A discharge-flow-tube technique has been used to measure the deactivation of HF(v=1,2). Effective vibrational deactivation rate constants for HF(v=1,2) relaxed by C₂H₄, C₂H₃F, 1, 1C₂H₂F₂, cis 1, 2C₂H₂F₂, trans 1, 2C₂H₂F₂, C₂HF₃, and C₂F₄ have been determined. For HF(v=1) the rate constants range from 4.9x10⁴ s⁻¹ torr⁻¹ for C₂H₄ to 3.5x10³ s⁻¹ torr⁻¹ for C₂F₄ and for HF(v=2) from 1.3x10⁵ s⁻¹ torr⁻¹ to 8.8x10³ s⁻¹ torr⁻¹. The cross sections for the deactivation of HF(v=1) and HF(v=2) by C₂H₄ and the fluoroethylenes are observed to scale linearly with the number of hydrogen atoms. (U)

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1.0 INTRODUCTION

With the increasing interest in and development of HF and DF lasers, numerous studies have been undertaken to supply the requisite information on both vibrational-vibrational and vibrational-translational deactivation of vibrationally excited HF and DF. The three principal experimental methods used were: laser-excited fluorescence (1,2), discharge-flow-tube (3,4) and "steady-state" chemiluminescence techniques (5). For the deactivation of HF by CO_2 , one of the few reactions studied by all three techniques, the agreement among the results obtained by these three techniques appears to be very good.

Very little attention has been given to the deactivation of HF by either fluorinated or unsaturated hydrocarbons. Anlauf et al (3) measured the rate of deactivation of $\text{HF}(v=1,2)$ by C_2H_4 to be $5 \times 10^4 \text{ torr}^{-1} \text{ s}^{-1}$ and $2.2 \times 10^5 \text{ torr}^{-1} \text{ s}^{-1}$ respectively. Bott and Cohen (1) obtained values of $(4.2 \pm 0.6) \times 10^2$, $(1.6 \pm 0.5) \times 10^2$, and $(6.3 \pm 1.0) \times 10^2 \text{ torr}^{-1} \text{ s}^{-1}$ respectively for the deactivation of $\text{HF}(v=1)$ by CF_4 , C_2H_6 , and C_4H_8 . Recent studies by Jones and Matinopoulous (6) of the infrared chemiluminescence produced by the reaction of H atoms with fluoroethylenes have prompted an interest in the rates of deactivation of $\text{HF}(v=1,2)$ by fluoroethylenes. Consequently, the present study using the discharge-flow-tube technique was undertaken to determine the rates of deactivation of $\text{HF}(v=1,2)$ by C_2H_4 and all the fluoroethylenes.

This work was performed at DREV during the latter half of 1976 under PCN 21T02 (formerly PCN 07301, Project No. 970139) "Research on Chemically Excited Lasers".

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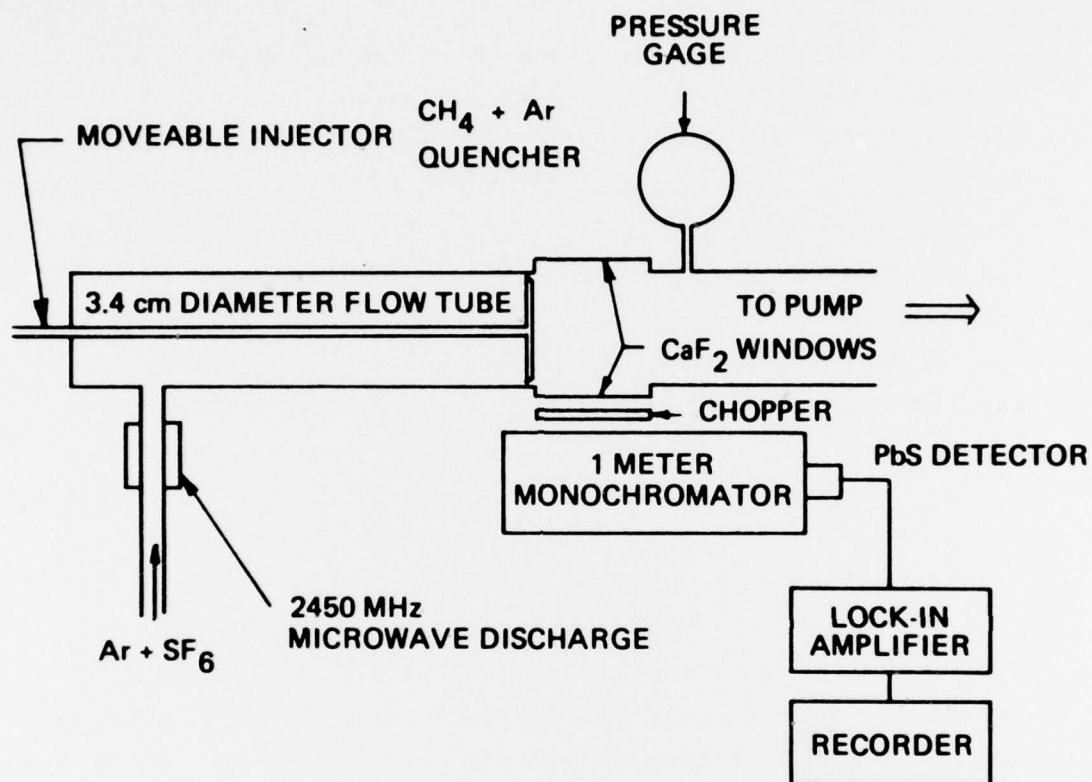


FIGURE 1 - Experimental Apparatus

2.0 EXPERIMENTAL

The experimental apparatus consisted of a medium-pressure (-1.7 torr) flow tube having a diameter of 3.4 cm (Figure 1). The F atoms were generated by passing SF_6 diluted with argon through a 2450 MHz microwave discharge in a 13-mm side arm. The discharge and the flow tube were both coated with phosphoric acid to inhibit atom recombination. The fuel, CH_4 , and the quencher along with additional argon were injected into the F atom argon stream by means of a moveable probe. This probe consisted of a glass tube with a teflon tip having four spokes with 16 holes of 0.25 mm diameter per spoke. The holes were oriented perpendicular to the flow axis. The probe position could be varied from the observation position to a point 15 cm upstream. Characterization of the flow was accomplished by measuring the pressure with a quartz spiral gauge (Texas Instruments) and the flow rates of the reactant gases with Fisher Porter flowmeters.

The detection system consisted of CaF_2 windows mounted flush with the walls of the flow tube, a McPherson 1 meter monochromator equipped with a dry-ice-acetone cooled PbS detector chopped at 200 Hz by a Bulova L8HH optical chopper and a Hewlett-Packard lock-in amplifier. The 2 mm slit of the chopper acted as an iris limiting the field of view. This gave a spatial resolution of 4.4 mm along the flow axis.

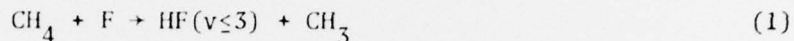
Typical experimental conditions were: molar flow rates (micromoles s^{-1}) Ar 884, SF_6 0.45, CH_4 5.24; pressure 1.65 torr; average linear velocity $1.85 \times 10^3 \text{ cm s}^{-1}$; temperature $(298 \pm 2)^\circ\text{K}$.

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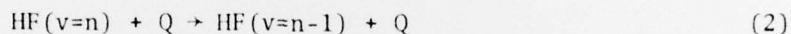
3.0 RESULTS AND DISCUSSION

Vibrationally excited HF is produced by the fast reaction



which has a rate constant $k = 5.48 \times 10^{-10} \exp(-575/T) \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ (7). The emission spectrum of the HF fundamental vibrational-rotational band is well resolved which permits the use of the $R_1(2)$ and $R_2(4)$ lines as a monitor of the $\text{HF}(v=1)$ and $\text{HF}(v=2)$ concentration.

$\text{HF}(v=n)$ is deactivated by the quenching reaction



where Q is the added quencher, as well as undergoing collisional deactivation with reactants and products, radiative decay and wall deactivation. The method of analysis employed is similar to that used by Kwok and Wilkins (8). The flow is treated as a fully developed, viscous, laminar, axially symmetric pipe flow having a parabolic radial dependence. Axial diffusion and coupling between $\text{HF}(v)$ levels are assumed to be negligible. Mixing of the reactants at the injector is assumed to be instantaneous. The value of the number density averaged along the tube diameter, \bar{N}_v , as a function of the radial coordinate z is approximately

$$\bar{N}_v(z) = \bar{N}_v(z=0) \exp(-z/\tau_v U') \quad (3)$$

where $\tau_v^{-1}(z)$ is the overall decay rate. The velocity U' compensates for the distortion of the density \bar{N}_v caused by the paraboloidal velocity profile. $U' = \phi \bar{U}$ where \bar{U} is the average velocity calculated from the continuity equation. The correction factor ϕ can be calculated for specified diffusion coefficients and given wall loss

conditions using the method outlined by Poirier and Carr (9). Figure 2 shows a typical plot of observed number density, \bar{N}_v , against distance along the z axis. The decay slopes obtained from these plots

$$\text{slope} = S_v = \frac{d(\ln \bar{N}_v)}{dz} = (\tau_v U')^{-1} \quad (4)$$

are then plotted against quencher concentration Q to give the quenching rate constant

$$\frac{dS_v}{dQ} = \frac{k_q}{U'} \quad (5)$$

Figure 3 shows a representative plot of S_v versus Q for the deactivation of HF($v=2$) by C_2H_6 .

The flow system was very steady during the measurements with changes in gas pressure and discharge parameters being less than 5%. The flows were steady to within 5% with the uncertainty in their absolute values calculated to be less than 20% of value. Detector sensitivity was sufficient to permit the decay of HF($v=1$) to be monitored over a distance of 10 cm and that of HF($v=2$) over a distance of 5 cm. The signal for \bar{N}_1 at the 1-cm position varied by less than 2% over 10 minutes and at the 10-cm position by less than 5%. As can be seen from Figure 2, the scatter about the least squares line drawn through the straight portion of the curve is small which permits an accurate determination of the slope. Similarly plots of S_v versus Q exhibit only small fluctuations from the expected linearity (Figure 3).

To test the experimental method and the assumptions made in the analysis, the rate of deactivation of HF($v=1$) by CH_4 , C_2H_6 and CO_2 was determined. The values of the rate constants obtained in the present study together with literature values are given in Table I.

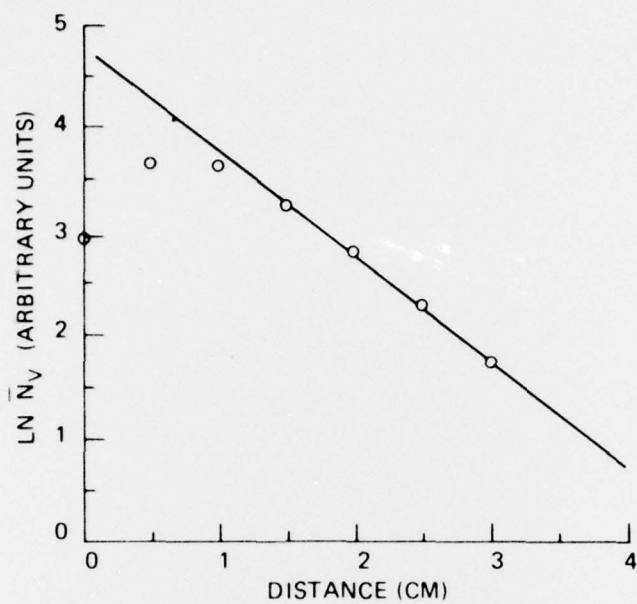


FIGURE 2 - Plot of observed number density, \bar{N}_V , against distance along the Z axis

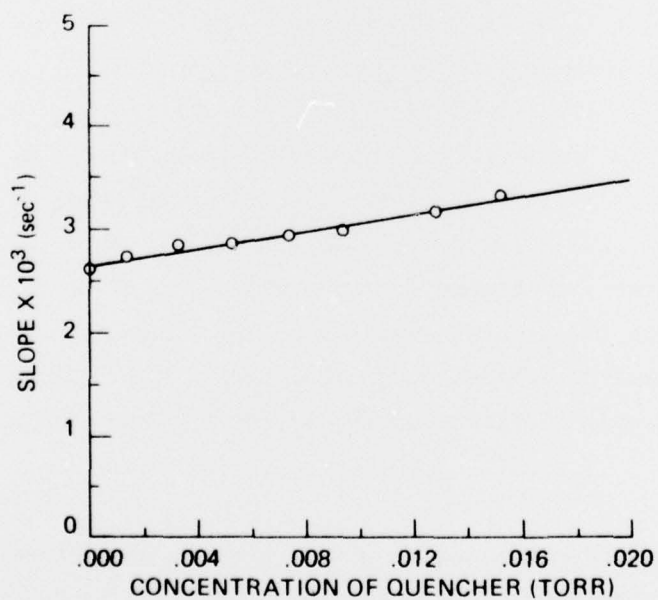


FIGURE 3 - Plot of S_V versus Q for the deactivation of HF($v=2$) by C_2HF_3

TABLE I

COMPARISON OF RATE CONSTANTS FOR THE DEACTIVATION OF HF($v=1$)
BY CH₄, C₂H₆ AND CO₂

Quencher	k_q (torr ⁻¹ s ⁻¹)	Method	Reference
CH ₄	3.5×10^4	discharge flow tube	present work
	2.1×10^4	discharge flow tube	Kwok & Cohen (4)
	6.4×10^4	discharge flow tube	Anlauf, Dawson & Herman (3)
	$(5.3 \pm 0.8) \times 10^4$	laser fluorescence	Hancock & Green (2)
C ₂ H ₆	9.3×10^4	discharge flow tube	present work
	$(1.1 \pm 0.16) \times 10^5$	laser fluorescence	Hancock & Green (2)
	5.6×10^4	discharge flow tube	Anlauf, Dawson & Herman (3)
CO ₂	4.0×10^4	discharge flow tube	present work
	4.1×10^4	discharge flow tube	Kwok & Cohen (4)
	$(3.6 \pm 0.2) \times 10^4$	laser fluorescence	Bott & Cohen (10)
	4.0×10^4	steady state chemiluminescence	Airey & Smith (5)
	$(5.9 \pm 0.2) \times 10^4$	laser fluorescence	Hancock & Green (11)
	$(4.25 \pm 0.6) \times 10^4$	laser fluorescence	Lucht & Cool (12)
	$(3.9 \pm 0.4) \times 10^4$	laser fluorescence	Bott (13)

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Good agreement with the literature values is obtained in the case of CO_2 and good agreement with the preferred value in the case of C_2H_6 . For CH_4 the present value lies intermediate between the two preferred values.

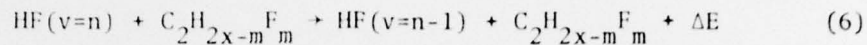
The rate of deactivation of $\text{HF}(v=2)$ by CH_4 and CO_2 was also determined. For CH_4 a value of $7.5 \times 10^4 \text{ torr}^{-1} \text{ s}^{-1}$ was obtained which is in reasonable agreement with the Kwok and Cohen (4) value of $6.9 \times 10^4 \text{ torr}^{-1} \text{ s}^{-1}$. For CO_2 , the value of $1.3 \times 10^5 \text{ torr}^{-1} \text{ s}^{-1}$ is somewhat lower than the values of $1.6 \times 10^5 \text{ torr}^{-1} \text{ s}^{-1}$ (4), $1.6 \times 10^5 \text{ torr}^{-1} \text{ s}^{-1}$ (5) and $(2.0 \pm 0.2) \times 10^5 \text{ torr}^{-1} \text{ s}^{-1}$ (13) obtained by other workers.

The rate constants for the deactivation of $\text{HF}(v=1)$ and $\text{HF}(v=2)$ by C_2H_4 and all the fluoroethylenes are given in Table II. Several determinations of each rate constant were made, six being the normal number with three being the minimum. The maximum deviation between values was 15% with the average deviation being considerably less. The values of the rate constants are considered to have uncertainties of less than a factor of 2 although the agreement between the values obtained for the deactivation of $\text{HF}(v=1)$ by CH_4 , C_2H_6 and CO_2 and the literature values indicate that the uncertainty is probably considerably less. The values of 4.9×10^4 and 2.2×10^5 obtained for the deactivation of $\text{HF}(v=1)$ and $\text{HF}(v=2)$ by C_2H_4 are thus in good accord with the approximate values of 5×10^4 and 2.2×10^5 given by Anlauf et al (3).

The cross section for the deactivation of $\text{HF}(v=1)$ and $\text{HF}(v=2)$ by fluoroethylenes ($\text{C}_2\text{H}_{2x-m}\text{F}_m$) appears to scale linearly with the number of hydrogen atoms ($2x-m$) which is equal to the number of CH stretching frequencies (Figures 4 and 5). Since the CH stretching frequencies for the fluoroethylenes fall within the range $3060 \pm 75 \text{ cm}^{-1}$, the energy defect, ΔE , for each member of the series of reactions

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is essentially the same, and the increased efficiency can be attributed to an increase in the number of CH stretching modes available. Hancock and Green (2) observed a similar dependence of collision cross section on the number of hydrogen atoms for the deactivation of HF($v=1$) by alkanes.

TABLE II

RATE CONSTANTS FOR THE DEACTIVATION OF HF($v=1,2$)
BY FLUOROETHYLENES

Quencher	$k_q (\text{torr}^{-1} \text{s}^{-1})$	
	HF($v=1$)	HF($v=2$)
C_2H_4	4.9×10^4	1.3×10^5
$\text{C}_2\text{H}_3\text{F}$	3.4×10^4	8.7×10^4
1,1 $\text{C}_2\text{H}_2\text{F}_2$	2.7×10^4	6.5×10^4
cis 1,2 $\text{C}_2\text{H}_2\text{F}_2$	3.1×10^4	5.9×10^4
trans 1,2 $\text{C}_2\text{H}_2\text{F}_2$	2.9×10^4	6.6×10^4
C_2HF_3	1.9×10^4	4.2×10^4
C_2F_4	3.5×10^3	8.8×10^3

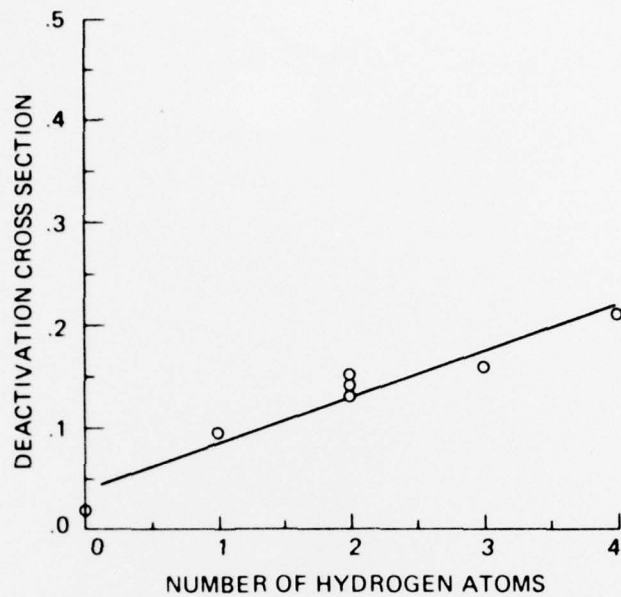


FIGURE 4 - Plot of deactivation cross section ($\sigma^2, \text{\AA}^2$) for HF(v=1) against number of hydrogen atoms in fluoroethylenes

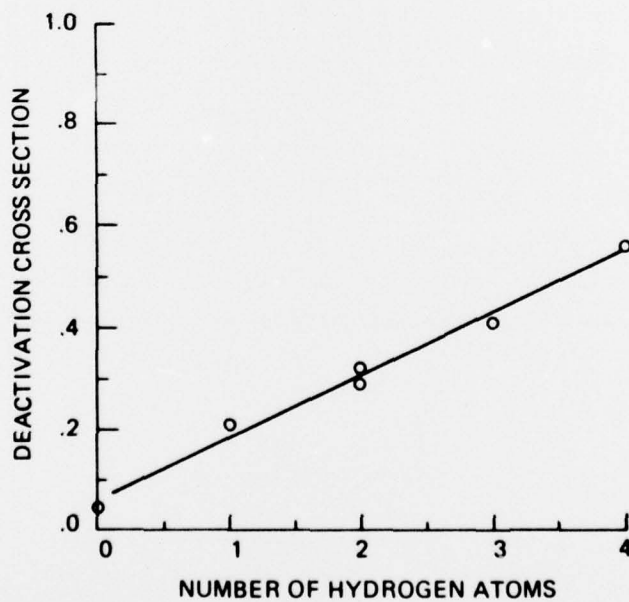


FIGURE 5 - Plot of deactivation cross section ($\sigma^2, \text{\AA}^2$) for HF(v=2) against number of hydrogen atoms in fluoroethylenes

4.0 CONCLUSIONS

A discharge-flow-tube method has been used to determine the rate of deactivation of HF(v=1) and HF(v=2) by CO₂, CH₄, C₂H₆, C₂H₄ and all the fluoroethylenes. The values of the rate constants obtained for the deactivation of HF(v=1) by CO₂, CH₄ and C₂H₆ are in good agreement with the literature values; it may therefore be concluded that the discharge flow tube method with the assumptions made in the analysis is capable of yielding satisfactory results. For the deactivation of HF(v=1) the value of the rate constants ranged from $4.9 \times 10^4 \text{ torr}^{-1} \text{ s}^{-1}$ for C₂H₄ to $3.5 \times 10^3 \text{ torr}^{-1} \text{ s}^{-1}$ for C₂F₄ and for HF(v=2) from $1.3 \times 10^5 \text{ torr}^{-1} \text{ s}^{-1}$ for C₂H₄ to $8.8 \times 10^3 \text{ torr}^{-1} \text{ s}^{-1}$ for C₂F₄. The cross sections for the deactivation of HF(v=1) and HF(v=2) by C₂H₄ and the fluoroethylenes are observed to scale linearly with the number of hydrogen atoms.

5.0 ACKNOWLEDGEMENTS

The authors wish to thank Mr. A. Blanchard for his assistance in the solution of the continuity equation.

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APPENDIX

The data was analysed in the manner described by Kwok and Wilkins (8) and Poirier and Carr (9). Consequently, only a brief resume of the method will be given here. The flow reactor is axially symmetrical with flow in the axial direction only. The reactions are assumed to occur isothermally in laminar flow. Thus, the differential equation describing the system is

$$-v_z \left(\frac{\partial C_i}{\partial z} \right) + D_i \left(\frac{\partial^2 C_i}{\partial r^2} + \frac{1}{r} \frac{\partial C_i}{\partial r} + \frac{\partial^2 C_i}{\partial z^2} \right) - R_i = 0 \quad (1A)$$

$i = 1, 2, \dots, n$

where v_z = axial velocity, z = axial coordinate measured from the reactor inlet, r = radial coordinate measured from the tube axis, C_i = concentration, D_i = molecular diffusivity, R_i = reaction rate of the i th component. When the velocity profile is described by Poiseuille's equation, axial diffusion is negligible in comparison to radial diffusion and when there is no volume change on reaction, equation 1A for an irreversible first order reaction is:

$$-v_o \left(1 - \left(\frac{r}{R} \right)^2 \right) \frac{\partial C}{\partial z} + D \left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} \right) - kC = 0 \quad (2A)$$

where v_o = center line velocity and R = tube radius. In demensionless form equation 2A is:

$$-(1-u^2) \frac{\partial C}{\partial \lambda} + \alpha \left(\frac{\partial^2 C}{\partial U^2} + \frac{1}{U} \frac{\partial C}{\partial U} \right) - C = 0 \quad (3A)$$

with $C = 1$ at $\lambda = 0$, $\partial C / \partial \lambda = 0$ at $U = 0$ and $-\alpha \partial C / \partial U = \beta C$ at $U = 1$; where $U = r/R$, $C = C/C_o$, $\lambda = k_z/v_o$, $\alpha = D/kR^2$ and $\beta = k_w/kR$. For a homogenous first order reaction with a concurrent first order wall

reaction, the parameter β in the boundary condition $-\alpha \partial C / \partial U = \beta C$ has positive values. The continuity equation, 3A, was solved using a finite difference technique. Concentrations were averaged along a principal diameter of the reactor

$$\bar{C}_1 = \int_0^1 C \, du \quad (4A)$$

and plots of $-\log \bar{C}_1 / C_0$ versus λ were obtained as a function of α and β as is done in reference 9. The slope, $-\log(\bar{C}_1 / C_0) / \lambda$ for the experimentally determined values of α and β , is ϕ , the correction to the average flow velocity required to compensate for the distortion of the number density, \bar{N}_v , caused by the parabolic velocity profile.

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